

APPENDIX

English translation of the specification of
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(Benz et al)

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(73) Patent holder: **Röhm GmbH**
64293 Darmstadt (DE)

(72) Inventors:

- **Dr. Volker Benz**
D-64739 Höchst (DE)
- **Michael Blumenstein**
D-64625 Bensheim (DE)
- **Georg Knoblauch**
D-81245 Munich (DE)
- **Peter Roche**
D-82275 Emmering (DE)

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EP-A- 0 318 797

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EP 0 589 343 B1**Description**

The invention concerns a three dimensionally formed tub or bowl shaped body of several plastic layers with a convex and a concave side, wherein the concave side consists of a layer of polymethyl methacrylate and the convex side consists of a reinforcing layer of rigid polyurethane plastic, and concerns a process for its production as well. Typical plastic bodies of this type are polymethyl methacrylate bath tubs reinforced with polyurethane foam.

State of the art

Known from GB-A 2 148 786 is a plastic bath tub body molded from a polymethyl methacrylate plate that is reinforced on its convex side with a layer of polyurethane foam. The only measure used by which to ensure adhesion of the polyurethane foam layer to the polymethyl methacrylate is the recommendation of degreasing the tub side subject to coating.

In practice, the adhesion of the polyurethane foam layer has proven to be insufficient when it is applied by spraying process onto the back side of the polymethyl methacrylate tub body. Under mechanical and thermal stress, for example, when the tubs are filled with hot water or when the transition spots of the tub floor edges are stepped on, such tubs can display the occurrence of high stresses and shearing forces on the narrowly restricted spots between the bound layers. On such spots, the foamed material layer can become detached from the polymethyl methacrylate layer and with added stress, the detachment can spread under continued stress until breakage results from insufficient rigidity.

According to the patent EP-A 211 495, the detachment of the foamed material layer is avoided if water is used as a foaming/expanding agent instead of a halogenated hydrocarbon. However, water reacts with the isocyanate groups of the isocyanate resin used to form the polyurethane foam layer and thus exercises a distinct influence on the properties of the polyurethane. Therefore one cannot freely select the quantity of water to achieve the desirable foaming results without simultaneously altering the characteristics of the polymeride.

By this measure as well, the risk of having the foamed material layer detach is obviously not reduced to a satisfactory level, because in the patent EP-A 304 187, the same patent holder suggested that the plastic layer to be reinforced with the foamed material layer be provided with nucleophilic groups which react with the isocyanate resin in order to further improve the adhesion. During the production of polymethyl methacrylate plates in accordance with the casting process, the nucleophilic groups are incorporated into the basic monomer mixture, in the form of hydrophilic co-monomers or of additives. This signifies a far reaching change in the production process of polymethyl methacrylate plates which can lead to their behavioral changes, such as for example toward water, and to problems during the production resulting from a changed adhesive behavior of the polymeride on the glass walls of the polymerization chamber.

Known from patent US-A 4,177,099, is the application of an adhesion providing layer of polyurethane, solute in chloroform, onto a stretched acrylic glass plate and to bond the coated

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side, under high pressure and at high temperature together with a prefabricated clear plate or foil made of polyurethane plastic. Polyurethanes with a high crystallization tendency are unsuitable as bonding agents. As a solvent, chloroform has the drawback of having a corrosive effect on the acrylic glass plate.

It is the objective of the invention to ensure a durable bond between the polymethyl methacrylate layer and the reinforced polyurethane plastic layer of bowl or tub shaped bodies, without altering the production process of polymethyl methacrylate plates and without limiting the selection of the foaming/expanding agent for the reinforcing polyurethane layer. The effect of corrosive agents on the acrylic glass shall be avoided at the utmost.

In the case of the generic process, it was found that this objective, in which a reinforcing layer of a reactive isocyanate resin was applied to the convex side of the polymethyl methacrylate layer which hardens to become a rigid polyurethane plastic, is achieved when the convex side of the polymethyl methacrylate layer is coated with a solution of a basically non-crosslinked, elastic polymer resin with strong crystallization tendency, with a softening temperature not under 50°C, with urethane-, ester- and/or hydroxyl groups in methoxy propanol and/or butyl acetate and possibly acetone as solvent/s and that after drying of the coating, the reinforcing layer of reactive isocyanate resin is applied and cured.

In accordance with the invention, the three dimensionally formed tub or bowl shaped bodies of several plastic layers with one convex and one concave side, are characterized, as a rule, in that between the polymethyl methacrylate layer and the polyurethane plastic layer, in contact with the latter two, a thinner layer of an elastic polymer resin with urethane-, ester-, and/or hydroxyl groups is arranged which is at least partially soluble in a solvent mixture of methoxy propanol, butyl acetate and possibly acetone. The layer can be cross linked at the surface of contact with the polyurethane plastic and thus be insoluble in part. If cross linking additives are jointly used during the production of the intermediary layer, which is possible, but not necessary, then the layer can be entirely insoluble.

The idea of improving inadequate adhesion between two plastic layers by arranging a layer of sticky resin or adhesion promoting resin in between them is already known. The difficulty in the present case lies in that customarily used adhesive resins had to be soluble in organic solvents which exercised a highly corrosive effect on the polymethyl methacrylate. Resins which are soluble in non-corrosive solvents, such as for example in aliphatic hydrocarbons, proved to be unsuitable for improving adhesion.

Surprisingly, certain elastic polymer resins with urethane-, ester- and/or hydroxyl groups proved to be soluble in a solvent mixture of methoxy propanol, butyl acetate and possibly acetone that is not very corrosive for polymethyl methacrylate when applied in the form of a polymer solution and dried. At a mixture ratio of 20 : 60 : 20 weight parts of the above components, no crack formation and no clouding of the coated polymethyl methacrylate surface was observed. Linearly constructed polymer resins are best soluble in organic solvents. Solubility decreases with the increasing branching and/or cross-linkage of polymer molecules. For the purpose of the invention, it suffices if a clear polymer solution can be produced and

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applied to become a uniform layer, even if the solution should have a colloidal state in part.

It was found that certain elastic polymer resins with urethane-, ester- and/or hydroxyl groups exercise a good adhesion mediating effect between the polymethyl methacrylate layer and the polyurethane layer and in addition to this, are soluble in the aforementioned solvent mixture. Based on this insight, the possibility emerged of providing the three dimensionally formed tub or bowl shaped bodies of polymethyl methacrylate with a layer of an elastic polymer resin with urethane-, ester- and/or hydroxyl groups, and to apply on top of that a durably adhering reinforcing layer of a rigid polyurethane plastic.

Upon determining damage stress in the stress corrosion test, whose execution is more closely detailed in the exemplified embodiment, it can be shown by the formation of cracks whether the polymethyl methacrylate layer is weakened by the application of the solution. With a damage stress of at least 12 N/mm^2 for the acrylic glass facing the polymer solution, or preferably of at least 14 N/mm^2 , the resulting multilayer material can be considered to be basically free of cracks.

Execution of the invention

The production of three dimensionally formed, tub or bowl shaped bodies, such as bath tubs or shower units of polymethyl methacrylate plates is generally known. For this, one mostly uses so-called "cast" acrylic glass which is produced by polymerization of methyl methacrylate in a flat chamber constructed of two glass plates and has a molecular weight high enough to pass over into a rubber like, elastic state when heated above the softening temperature, but which does not melt upon further heating. Recently, extruded plates of thermoplastic polymethyl methacrylate molding compound have also been used for this purpose. Both types of plates are heated up to the thermoelastic state and are formed three dimensionally by means of positive or negative forming tools and are set into their assumed shape by cooling down to below the softening temperature.

The concept of polymethyl methacrylate includes co-polymerides which, in addition to the methyl methacrylate as the main ingredient, contain limited amounts of mixed polymerizable co-monomers. As a rule, the moiety of methyl methacrylate lies at above 80%, preferably at above 90 weight % relative to the weight of the polymeride. Plates of 3 to 10 mm in thickness are generally used which have dye pigments in them.

The concave side of the three dimensionally formed body is the showing side or the user side. The convex back side is coated with the solution of elastic polymer resin with urethane-, ester and/or hydroxyl groups and is dried to become a solid protective layer. Polymer solutions with a resin content of 0.5 to 30 weight percent, preferably 1 to 15, and especially with 3 to 8 weight percent are suitable.

The elastic, urethane-, ester- and/or hydroxyl group containing polymer resins differ in view of their crystallization tendency which manifests itself by the temperature at which they soften. Resins with high crystallization tendency have softening temperatures that are not below 50°C

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and possibly go up to 80°C or above. These resins are used for the invention, while non-crystalline resins with softening temperatures of about 45°C or below can lead to the formation of stress cracks and are therefore unsuitable.

Preferred polymer resins are linear hydroxyl polyester polyurethanes which are developed by the transformation of a part of the hydroxyl groups of a polyester polyol with a diisocyanate under the formation of urethane groups. In this series of resins, those with strong crystallization tendency are especially well suited. Typical solution viscosities, measured in 15% solutions in methyl ethyl ketone at 23°C, lie at about 1 - 2 Pa s (Brookfield viscometer LVF, spindle 3, 60 rev./min.). A suitable polymer resin solution is commercially offered by Röhm GmbH, under the designation "Grundierung 60" (filling material 60).

Other polymer resins with urethane-, ester- and/or hydroxyl groups can be selected by their solubility in the above mentioned solvent mixture and by their softening temperature. The named groups work advantageously for the adhesive characteristics onto the polymethyl methacrylate and onto the polyurethane plastics so that the resins containing all three of the named groups are especially preferred. Polymer resins with urethane and ester groups without hydroxyl groups or with ester and hydroxyl groups without urethane groups are equally usable in many cases. It is advantageous, even if not compulsory, if the ester groups are positioned in the backbone chain of the polymer resin.

The solvent mixture for the production of the adhesion mediating intermediate layer of elastic polymer resin contains preferably 60 weight parts of butyl acetate and respectively 20 weight parts of acetone and methoxy propanol.

The polymer resin solution can be applied onto the polymethyl methacrylate layer by any normal coating technique, preferably by spraying. The required thickness depends on the concentration. The coating can be dried at room temperature or at a slightly higher temperature, possibly under an air stream.

The reinforcing layer of polyurethane plastic can be applied onto this coating. Resin systems suitable to this end are known and commercially available. As a rule, they contain at least one polyol, preferably one polyester polyol, and at least one polyfunctional isocyanate which reacts with the polyol by formation of a cross-linked polymer matrix, and possibly some hardening catalysts and other additives. It is essential that the mixture cures at room temperature to become a rigid non-elastic polyurethane plastic.

To the extent that water or expanding/foaming agents are jointly used as additives, a more or less highly foamed polyurethane plastic layer will form. Its density lies preferably in the range of 0.2 to 1.0 KG/m³. Furthermore, it can contain filler materials such as minerals or fibrous materials, specifically glass fibers, at a quantity of 5 to 40 weight percent for example, relative to the total weight of the reinforcing layer.

The required thickness of the reinforcing layer depends on the size and shape of the three dimensionally formed body. For bath tubs, a layer thickness of 5 to 20 mm is suitable; for shower units and bodies of comparable size and capacity to withstand comparable loads, 3 to 10 mm will usually suffice. The reinforcing layer can be constructed to be thicker at highly stressed

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points than at other points undergoing lesser stress.

The resin mixture of polyol and polyisocyanate and possibly of additives is preferably applied onto the coated, convex side of the tub or bowl shaped body by means of a two material mixing nozzle, whereby curing sets in very rapidly. It already begins in the mixing nozzle and it is completed within a few seconds or minutes after being spraying on at temperatures of 20° to 30°C.

In a preferred embodiment of the invention, the reinforcing layer of polyurethane plastic is produced in several layers on at least one part of the surface of the three dimensionally shaped body. Immediately after the first layer, a second layer can be applied until the desirable thickness is attained after two to five spraying runs. An especially highly rigid effect of the reinforcing layer is achieved with a low quantity of application material if a slightly foamed or non-foamed polyurethane layer is applied as the first coat, then evermore foaming layers are applied up to the middle of the reinforcing layer, and after that layers with higher densities are once more produced. In practice, a three coat construction has proven to be durable: The first and the third coat are about the same with densities of 0.8 to 1.0 KG/m³, and included in between that is a foamed coat with a density of 0.1 to 0.5 KG/m³.

Example 1

A bath tub is formed from a 5 mm thick plate of cast acrylic glass, at a thermoelastic temperature range, and with a weight of 8.8 KG. On the convex back side, a 6 weight % solution of a hydroxyl polyurethane (commercial product "Grundierung 60" (filling material 60), Röhm GmbH) in a solvent mixture of 60 weight % butyl acetate, 20 weight % acetone and 20 weight % methoxy propanol is evenly sprayed on and left to dry at room temperature. After this, 1.4 KG of a high density polyurethane resin system (commercial product RMS - System "Elastocoat C 6816 - 80 - M" from the Elastogran Polyurethane GmbH firm, Olching) is applied while lightly favoring the tub floor area, whereby a median coat thickness of about 2 mm is obtained. Immediately after this, 2.2 KG of a "polyurethane - solid foam system" (commercial product RSM - System "Elastocoat C6812" by the Elastogran Polyurethane GmbH firm, Olching) is applied which results in a density of 600 KG/m³ and a median coat thickness of about 10 mm. As the last coat, 1.8 KG of the polyurethane resin system used for the first coat is once more applied.

The reinforced bath tub has an overall weight of 15.4 KG. A damage stress of 17 N/mm² on the processed acrylic glass was determined for the described composition of polymer resin solution. The reinforced bath tub complies with the requirements of the European Norm EN 198 for bath tubs made of acrylic glass. With a conventional glass fiber reinforced plastic, this utility strength is just attained at an overall weight of 20 KG.

To determine the damage stress in the stress corrosion test, a strip shaped test body of uncoated acrylic glass with a length of 230 mm, a width of 20 mm and a thickness of 4 mm is

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horizontally clamped down at one end and is stressed by a weight hanging from it at the other free end so that in proximity to the clamping point, a maximum tensile stress (σ_{maximum}) of 30 MPa occurs. The tensile stress on the test body diminishes linearly down to zero at the load distribution point so that each point on the upper surface can be assigned a defined tensile stress value in relation to its distance from the clamping point. The surface of the test body is coated with the polymer resin solution and left to dry. Crack formation begins at the site of the highest tensile stress at the clamping point and progresses with the duration of testing in the direction of the decreasing tensile stress. After 24 hours at 50°C, the damage stress is designated by the end of the crack formation zone (σ_{limit}).

Example 2

A bath tub body with a weight of 8.6 KG is coated as in example 1. The reinforcing coat is produced only from the polyurethane solid foam system (commercial product RSM - System "Elastocoat C6812" by the Elastogran Polyurethane GmbH firm, Olching) in that 8.0 KG of the resin with formation of a foamed material is applied in several layers with a density of 600 KG/m^3 , and with an overall thickness of 15 to 20 mm. The total weight of the reinforced tub amounts to 16.6 KG.